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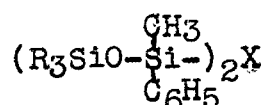
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"A Study of the Properties of Polymers with Alternating Siloxane and Sil-Phenylene Linkages," T.I.Ponomareva, T.A.Krasovskaya and M.V.Sobolevskii, *Plasticheski Massy*, (No. 6) 21 (1964)

In this contribution there is reported work pertaining to the investigation of the relationships between bis-(triorganosilyl)-benzenes and hexaorganodisiloxanes. In the present work, results were obtained using mixtures of compounds with recurring silphenylene units in the molecule.

The methods of hydrolytic condensation of condensation of triorganochlorosilanes with bis-(methylphenylchlorosilyl)-benzenes or with methylphenyldichlorosilane and subsequent rearrangement to mixed polymers gave the general formula



where R is phenyldimethyl or methylphenyl and X is oxygen or phenylene.

In Table 1 will be found the general characteristics of the four polymers.

As seen in Table 1, polymers with benzene rings in the chain have higher temperatures of congealing than do the analogous organosiloxanes.

Table 1, Characteristics of Organosiloxanes and of Organophenylenesiloxanes

	A.	B.	C.	D.
1. $(\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{O})_2\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_4$	-12.0°	25.4cs	835	618
2. $(\text{C}_6\text{H}_5\text{Si}(\text{CH}_3)_2\text{O})_2\text{Si}(\text{CH}_3)_2$	-46.0°	6.4cs	777	558
3. $(\text{CH}_3\text{Si}(\text{C}_6\text{H}_5)_2\text{O})_2\text{Si}(\text{CH}_3)_2$	+17.9°	92.5cs	1048	1074
4. $(\text{CH}_3\text{Si}(\text{C}_6\text{H}_5)_2\text{O})_2\text{Si}(\text{CH}_3)_2$	-18.0°	23.3cs	964	954

- A Congealing Temperature (brittle point ?)  
 B Viscosity  
 C Molecular Weight, Found  
 D Molecular Weight, Calculated

The viscosity of organophenylenesiloxanes changes more sharply with respect to temperature than does that of organosiloxanes. In the interval between 250° and 100° C., the viscosity of organosiloxanes changes about 4 to 8 fold, the viscosity of organophenylenesiloxanes 10 to 18 fold (figure 1).

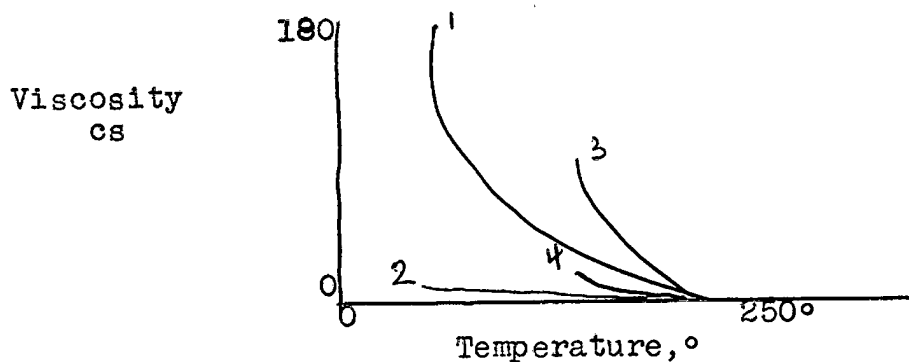


Figure 1

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Compounds with aromatic rings in the polymeric chains show less resistance (stability) to thermooxidation than (do) the organosiloxanes. With thermooxidation (300° C., passing air across the polymer surface) polymers 1 and 3 over 30 hours turn to a gel, and polymers 2 and 4 remain in the liquid state. Their viscosities increase, however, from 3.0 to 41.5 fold (Table 2).

Table 2

Change in Viscosity of Organophenylenesiloxanes and of Organosiloxanes during the Process of Thermooxidation at 300° C.

	Initial Viscosity 100° C., cs	Change in viscosity, with time, hrs., cs					
		10	20	30	50	70	100
1	25.43	41.5	1704			Gel	
2	6.4	8.2	10.0	11.8	14.0	20.0	29.1
3	92.5	484.0	1770			Gel	
4	23.3	26.8	-	37.8	41.3	58.6	69.0

At 250° C., during the thermooxidative process the weight loss of organophenylenesiloxanes is slightly higher than (that of) organosiloxanes. In the case of heating the polymers in an atmosphere of nitrogen, correlation of weight loss shows the reverse, from the curve, plotting against time. Polymer 3 has amore strongly polar character

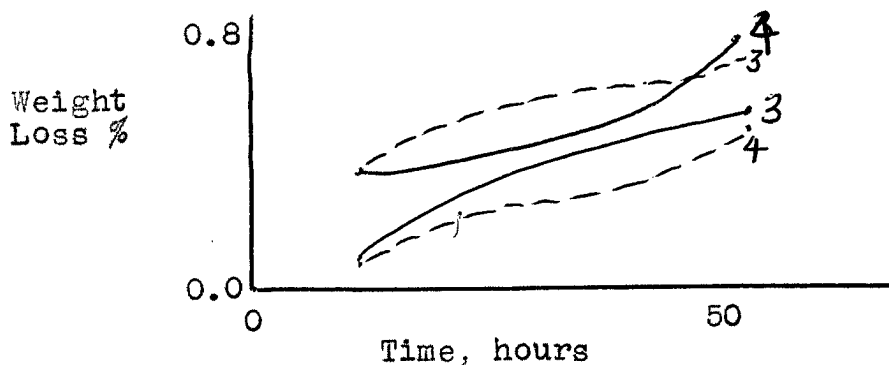


Figure 2, Loss of weight at 250°C. when heated in air (----) and in nitrogen (solid line), curves for polymers 3 and 4.

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The temperature of decomposition (measured as change in elasticity) of organophenylenesiloxanes at 120°-130° C. is higher than for organopolysiloxanes and measures, for polymers 1 and 3, 442° and 443° C., for 2 and 4, 281° and 316° C.

Specifying apparatus KT-2, lubricating data on all four polymers are about identical. For the characterization of organophenylene-siloxanes there is an absence of extensive data on the coefficient of friction. The value for this coefficient is 0.2 or 0.28 for the temperature interval 100°-300° C. For organosiloxanes the coefficient of friction is 0.19 to 0.4. The diameter loss for all four polymers is 0.15 to 0.16 mm in the interval 100°-300° C.

#### Summary

1. The introduction of the benzene ring into a molecule of methylphenylsiloxane increases the viscosity, the temperature coefficient of viscosity and heightens the temperature of setting.
2. Replacement of oxygen between silicons by the benzene ring lowers the thermooxidative resistance of the methylphenylsiloxane but improves the thermal resistance.
3. Organophenylenesiloxanes have a temperature of decomposition of 120°-160° above that of organosiloxanes.
4. The introduction of the benzene ring into the molecule of a methylphenylsiloxane practically speaking, has no effect on the lubricating properties.

#### Literature

T.I. Ponomareva, T.A. Krasovskaya and M.V. Sobolevskii,  
Plasticheskie Massy, (No. 7) 22 (1963)

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